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UMBRAL CALCULUS AND THE THEORY OF MULTISPECIES NONIDEAL GASES

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1).Introduction

The traditional expostulation of the statistical mechanics of non-ideal gases starts with the fugacity expansion of the grand potential

$$\Xi = \sum Q_{\underline{N}} \underline{\lambda}^{\underline{N}}$$

introduces the concept of reducible cluster coefficients $b_{\underline{n}}$ via the activity expansion

$$\frac{P}{KT} = \sum b_{\underline{N}} \underline{Z}^{\underline{N}}$$

and by use of the thermodynamic relations

$$\frac{PV}{KT} = \ln \Xi \qquad \bar{N}_{\sigma} = \left(\frac{\partial}{\partial \mu_{\sigma}} \ln \Xi \right)_{T,V}$$

obtains the density expansion of the pressure

$$\frac{P}{KT} = \underline{D}\cdot\underline{1} - \sum (\underline{N}\cdot\underline{1} - 1) B_{\underline{N}} \underline{D}^{\underline{N}}$$

For a one species gas the virial expansion was derived by Kahn[1] using the Lagrange-Burmann inversion formula.[2] A modern treatment for the multispecies gas is given by Friedman[3] utilizing generating functions to count Hussimi trees.[4] The relationship betwee the $b_{\underline{n}}$ and the $\underline{n}$ body partition functions $Q_{\underline{n}}$ (eigther classical or quantum mechanical), and more importantly between the irreducible cluster coefficients $B_{\underline{n}}$ and the reducible cluster coefficients $b_{\underline{n}}$,were first given by Mayer[5] and Kilpatrick[6] for a one species gas by involved combinatoric countings. The virial expansion and the $b_{\underline{n}}$ in terms of $B_{\underline{n}}$ for a multispecies gas was first given by Mayer[7] and Fuchs[8] using extensive, intricate combinatorics and multivariate complex contour integrations. (The inverse relationship for the multispecies case has heretofore never been given.)

This heavy reliance on an armada of graph theory,combinatorics and complex variable analysis unnecessarily complicates the theory. It will be shown here that the Umbral calculus-the algebra of formal series-is a natural format to use instead. With it all the relations (both for the single species and multispecies case) are derived from a simpler unified framework. Unlike manipulations traditionally derived from graph theory,combinatorics or complex variable analysis, the umbral developement is algebraic and therefore adaptable to computer algorithms. Furthermore it is easy to master and exploit because it employs the Dirac notation familiar from quantum mechanics. Most of the concepts (dual space, adjoint operators, etc.) carry over unchanged.

This paper consists of eight parts. In section two we highlight the pertinent portions of the theory of multivariate umbral calculus. Section three presents an algebraic derivation of the single and multivariable Lagrange inversion formulas. In section four the relations between the reducible cluster coefficients and the $\underline{n}$ body partition functions for both a single and multispecies gas is presented from the Umbral viewpoint. Sections five and six contain the umbral derivation of the virial expansion and the relations between the reducible and irreducible cluster coefficients for a single species non-ideal gas,while sections seven and eight are the generalizations encompassing the multispecies case.

2).Theory

The theory and notation presented here is loosely based on an excellent series of articles by Roman.[9] Readers interested in a rigorous developement of the subject are urged to refer to these. The intention here is to present a quick intuitive grasp of the necessary tools.

Define Bra space as the space of all formal series in the objects $A_\alpha, A_\gamma, \ldots, A_\mu$ of the form

$$Q = \sum_{\underline{i}=[Q]}^{\infty} a_{\underline{i}} \underline{A}^{\underline{i}}$$

Symbols with a bar underneath always denote vector quantities, for example the index

$$\underline{i} \equiv (i_\alpha, i_\gamma, \ldots, i_\mu)$$

We adhere to the standard shorthand notation

$$\underline{A}^{\underline{i}} = (A_\alpha{}^{i_\alpha})(A_\gamma{}^{i_\gamma})\ldots(A_\mu{}^{i_\mu})$$

The vector [Q],called the degree of Q, is equal to $\underline{i}$ of the lowest nonvanishing term. Elements in Bra space are denoted by upper case letters. We stress that this is a formal series because the $\underline{A}^{\underline{i}}$ are not variables. Rather it is intuitive to think of Q as a quantu state expanded in a set of basis states $\underline{A}^{\underline{i}}$.

Ket space is the space of all formal series in the objects $x_\alpha, x_\gamma, \ldots, x_\mu$ of the form

$$q = \sum_{-\infty}^{\underline{j}=[q]} b_{\underline{j}} \underline{x}^{\underline{j}}$$

The vector [q], called the degree of q, is equal to $\underline{j}$ of the highest nonvanishing term. Elements in ket space are denoted by lower case letters.

Brackets are defined by the action

$$\langle Q | q \rangle = \sum_{\underline{i}} \sum_{\underline{j}} a_{\underline{i}} b_{\underline{j}} \langle \underline{A}^{\underline{i}} | \underline{x}^{\underline{j}} \rangle$$

where the $\underline{A}^{\underline{i}}$ and the $\underline{x}^{\underline{j}}$ form a biorthogonal set

$$\langle \underline{A}^{\underline{i}} | \underline{x}^{\underline{j}} \rangle = c_{\underline{i}} \, \delta_{\underline{i}\underline{j}}$$

Here the vector indexed Kronecher delta is defined by

$$\delta_{\underline{i}\underline{j}} = (\delta_{i_\alpha j_\alpha})(\delta_{i_\gamma j_\gamma})\ldots(\delta_{i_\mu j_\mu})$$

and the connection constants $c_{\underline{i}}$ are arbitrary at this point but will be chosen later to advantage.

Bra elements are commutative and associative and satisfy the product theorem

$$\langle QR|\underline{X}^{k}\rangle = \sum_{i} \frac{c_k}{c_i\, c_{k-i}} \langle Q|\underline{X}^{i}\rangle\langle R|\underline{X}^{k-i}\rangle$$

The extension to multiple products follows easily by induction.

In multivariate umbral calculus our concern is rarely with a single bra element, say L , but rather with a set of bra elements $L_\alpha, L_\gamma, \ldots, L_\mu$ from which we form the vector

$$\underline{L} = (L_\alpha, L_\gamma, \ldots, L_\mu)$$

whose components are of the form

$$L_\sigma = A_\sigma + H_\sigma$$

where H_σ is eigther zero or whose degree is of magnitude two or more (that is, the lowest nonvanishing term is of the form $a_{20}A_\alpha^2$ or $a_{11}A_\alpha A_\gamma$ or the like). We call such objects delta sets. Delta sets have two important properties; any formal series in $\underline{A}^{\underline{i}}$ can be written as a formal series in $\underline{L}^{\underline{i}}$ and they have unique compositional inverses.

The composition operation is defined as occuring between a single bra element

$$F = \sum_{i} f_i\, A^{i}$$

and the delta set vector

$$\underline{L} = (L_\alpha, L_\gamma, \ldots, L_\mu)$$

(of which each component is a bra element,ie a formal series in $\underline{A}^{\underline{i}}$) and is defined by the action

$$F \bullet \underline{L} = \sum_{i} f_i\, \underline{L}^{\underline{i}}$$

A delta set vector $\underline{L}$ has a compositional inverse $\underline{\tilde{L}}$ which is also a delta set vector. By compostional inverse we mean

$$L_\sigma \bullet \underline{\tilde{L}} = A_\sigma = \tilde{L}_\sigma \bullet \underline{L}$$

for all component indices σ .

We wish to generalize the idea of the biorthogonality between the vector powers of the delta set vector $\underline{A}$ and the vector indexed sequence of ket elements

$$a_{\underline{i}} \equiv \underline{X}^{\underline{i}}$$

to encompass any delta set vector $\underline{F}$. To that end we can uniquely define an associate sequence to $\underline{F}$ as a vector indexed sequence of ket elements

$$f_{\underline{i}} = \sum_{\underline{k}=-\infty}^{\underline{i}} g_{\underline{k}} \underline{x}^{\underline{k}}$$

such that

$$< \underline{F}^{\underline{i}} | f_{\underline{j}} > = c_{\underline{i}} \, \delta_{\underline{ij}}$$

and which, like the $a_{\underline{j}}$,satisfies the product property

$$<QR | f_{\underline{j}} > = \sum^{\underline{j}} \frac{c_{\underline{j}}}{c_{\underline{k}} \, c_{\underline{j}-\underline{k}}} <Q | f_{\underline{k}} > < R | f_{\underline{j}-\underline{k}} >$$

By invoking the spanning postulate, which states

I). $< \underline{L}^{\underline{k}} | q > = < \underline{L}^{\underline{k}} | r >$ for all $\underline{L}^{\underline{k}}$ implies q=r

II). $< F | 1_{\underline{n}} > = < G | 1_{\underline{n}} >$ for all $1_{\underline{n}}$ implies F=G

it follows that any bra space element M may be expanded in term of any other delta set vector $\underline{L}$ as

$$M = \sum^{\underline{j}} \frac{<M | \ell_{\underline{k}}>}{c_{\underline{k}}} \underline{L}^{\underline{k}}$$

This is known as the expansion theorem.

A mapping from the ket element $\underline{x}^{\underline{n}}$ to the ket element $f_{\underline{n}}$ is accomplished by a noncommutative operator called the transfer operator, denoted by

$$f_{\underline{n}} = \left\{ \frac{\underline{F}}{\uparrow} \right\} \underline{x}^{\underline{n}}$$

To each operator in ket space is an adjoint in bra space which maps bra elements into bra elements. The adjoint is denoted by flipping the labels in the brace. An adjoint has the property

$$< Q | \left\{ \frac{\underline{F}}{\uparrow} \right\} r > = < \left\{ \frac{\uparrow}{\underline{F}} \right\} Q | r >$$

The adjoint of an inverse is the inverse of the adjoint.

The adjoint of the transfer operator has the action

$$\underline{L}^{\underline{k}} = \left\{ \frac{\uparrow}{\underline{L}} \right\}^{-1} \underline{A}^{\underline{k}}$$

and the transfer operator for a composite of two delta set vectors can be expressed as a product of transfer operators

$$\left\{ \frac{\underline{L} \bullet \underline{M}}{\uparrow} \right\} = \left\{ \frac{\underline{M}}{\uparrow} \right\} \left\{ \frac{\underline{L}}{\uparrow} \right\}$$

It follows that the compositonal inverse to $\underline{F}$, which has its own associate sequence

$$\tilde{f}_{\underline{N}} = \left\{\frac{\tilde{F}}{\uparrow}\right\} \underline{x}^{\underline{N}}$$

is directly related to $\underline{F}$ via

$$\tilde{f}_{\underline{N}} = \sum_{\underline{K}=-\infty}^{\underline{N}} \frac{\langle F^{\underline{K}} | \underline{x}^{\underline{N}} \rangle}{c_{\underline{K}}} \underline{x}^{\underline{K}}$$

and so is called the conjugate sequence to $\underline{F}$. The relationships between the sequences and the delta set vectors are easily summarized diagramaticly :

$$\begin{tikzcd}
& F \arrow[dl, "\text{CONJUGATE}"'] \arrow[dr, "\text{ASSOCIATE}"] & \\
\tilde{f} & & f \\
& \tilde{F} \arrow[ul, "\text{ASSOCIATE}"] \arrow[ur, "\text{CONJUGATE}"'] &
\end{tikzcd}$$

Two other operators form the backbone of the umbral calculus. The creation operator is defined by the action

$$\langle F G | \underline{x}^{\underline{L}} \rangle = \langle F | \left\{\frac{G}{\circledast}\right\} \underline{x}^{\underline{L}} \rangle$$

From the product theorem we see that in ket space the operator has the action

$$\left\{\frac{G}{\circledast}\right\} \underline{x}^{\underline{L}} = \sum^{\underline{1}} \frac{c_{\underline{L}}}{c_{\underline{1}}\, c_{\underline{L}-\underline{1}}} \langle G | \underline{x}^{\underline{L}-\underline{1}} \rangle \underline{x}^{\underline{1}}$$

Because the creation operator is commutative and has the property

$$\left\{\frac{\underline{M}}{\circledast}\right\}^{\underline{K}} \equiv \left(\left\{\frac{M_1}{\circledast}\right\}^{K_1}\right)\left(\left\{\frac{M_2}{\circledast}\right\}^{K_2}\right)\dots\left(\left\{\frac{M_n}{\circledast}\right\}^{K_n}\right) = \left\{\frac{\underline{M}^{\underline{K}}}{\circledast}\right\}$$

we have the specific action

$$\left\{\frac{\Delta}{\circledast}\right\}^{\underline{K}} \underline{x}^{\underline{L}} = \frac{c_{\underline{L}}}{c_{\underline{L}-\underline{K}}} \underline{x}^{\underline{L}-\underline{K}}$$

If we now specify that the connection coefficients $c_{\underline{k}}$ are given by

$$c_{\underline{K}} \equiv (c_{K_1})(c_{K_2})\dots(c_{K_n})$$

where

$$c_m = \begin{cases} m! & \text{FOR } m \geq 0 \\ \dfrac{(-1)^{m+1}}{[-(m)-1]!} & \text{FOR } m < 0 \end{cases}$$

Then like the ordinary derivitive $\frac{\partial}{\partial x_\sigma}$ we have

$$\left\{\frac{\Delta_\sigma}{\circledast}\right\} x_\sigma^{L_\sigma} = L_\sigma x_\sigma^{L_\sigma - 1} \qquad \text{FOR } L_\sigma \neq 0$$

while unlike the ordinary derivitive

$$\left\{ \frac{A_\sigma}{\bullet} \right\} x_\sigma^0 = x_\sigma^{-1} .$$

We choose this convention for its ability to treat formal series of positive and negative powers on a unified basis.

We can easily give a criterion for associated sequences in terms of the action of the creation operator: a sequence $f_{\underline{i}}$ is and associate sequence to the delta set vector $\underline{F}$ if and only if

$$\text{I).} \quad \left\{ \frac{\underline{F}}{\bullet} \right\}^{\underline{1}} f_{\underline{i}} = \frac{c_{\underline{i}}}{c_{\underline{i}-\underline{1}}} f_{\underline{i}-\underline{1}} \qquad \text{EQN 2.1}$$

$$\text{II).} \quad \langle \underline{A}^{\underline{k}} \mid f_{\underline{i}} \rangle = c_{\underline{i}} \delta_{\underline{i}\underline{k}} \qquad \text{EQN 2.2}$$

The last important operator, the derishift operator, is defined for delta set vectors in bra space as having the action

$$\left\{ \frac{\partial}{L_\sigma} \right\} \underline{L}^{\underline{k}} = k_\sigma \underline{L}^{\underline{k}-\underline{e}_\sigma}$$

where $\underline{e}_\sigma$ is the unit vector in the σ direction. From the expansion theorem we see that the derishift operator satisfies the Liebnitz rule

$$\left\{ \frac{\partial}{L_\sigma} \right\} QR = Q\left(\left\{ \frac{\partial}{L_\sigma} \right\} R \right) + \left(\left\{ \frac{\partial}{L_\sigma} \right\} Q \right) R$$

and the chain rule

$$\left\{ \frac{\partial}{L_\sigma} \right\} = \sum_\nu^{\cdot} \left(\left\{ \frac{\partial}{L_\sigma} \right\} M_\nu \right) \left\{ \frac{\partial}{M_\nu} \right\}$$

where the sum on ν runs over all component indices. With our choice of the connection coefficients the derishift operator in ket space has the action

$$\left\{ \frac{L_\sigma}{\partial} \right\} \ell_{\underline{i}} = (1 - \delta_{-1, i_\sigma}) \ell_{\underline{i}+\underline{e}_\sigma}$$

of shifting the index of the associate sequences.

3). The Transfer Formula

As a first application we will present the algebraic derivation of the Lagrange-Burmann formula for the inversion of a series in a single variable as well as the generalization encompassing the inversion of a set of series, each in many variables. Readers interested in the standard derivation by complex contour integration should refer to Whitaker and Watson[illegible] and Good.[10]

These formulas are an immediate consequence in umbral calculus of the transfer formula, which gives an explicit construction of the associate sequence directly from a knowledge of the delta set vector:

$$f_{\underline{i}} = \frac{c_{\underline{i}}}{c_{-\underline{1}}} \left\{ \frac{\Delta_\wedge E}{\otimes} \right\} \left\{ \frac{\underline{E}}{\otimes} \right\}^{-\underline{1}-\underline{i}} \underline{x}^{-\underline{1}}$$

where

$$\underline{\Delta}_\wedge E = \det \left(\left\{ \frac{\partial}{\partial A_\nu} \right\} F_\sigma \right)$$

To prove this theorem we note that the transfer formula trivially satisfies equation (2.1) and so we only need show that equation (2.2), equivalent to

$$\langle (\underline{\Delta}_\wedge E)\, \underline{E}^{-\underline{1}-\underline{i}} \mid \underline{x}^{-\underline{1}} \rangle = c_{-\underline{1}}\, \delta_{\underline{i},\underline{0}}$$

also holds. The proof is easily illustrated for three variables, the generalization to any dimension being apparant.

When only one of the i_σ (σ=1,2,3 for our three variable example) is non zero-say the first component i_1 (there is no loss of generality as the determinant will differ by at most a sign) we have

$$(\underline{\Delta}_\wedge E)\, \underline{E}^{-\underline{1}-\underline{i}} = \begin{vmatrix} \left\{ \frac{\partial}{\partial A_1} \right\} G_1 & \left\{ \frac{\partial}{\partial A_2} \right\} G_1 & \left\{ \frac{\partial}{\partial A_3} \right\} G_1 \\ \frac{1}{F_2} \left\{ \frac{\partial}{\partial A_1} \right\} F_2 & \frac{1}{F_2} \left\{ \frac{\partial}{\partial A_2} \right\} F_2 & \frac{1}{F_2} \left\{ \frac{\partial}{\partial A_3} \right\} F_2 \\ \frac{1}{F_3} \left\{ \frac{\partial}{\partial A_1} \right\} F_3 & \frac{1}{F_3} \left\{ \frac{\partial}{\partial A_2} \right\} F_3 & \frac{1}{F_3} \left\{ \frac{\partial}{\partial A_3} \right\} F_3 \end{vmatrix}$$

where

$$G_\sigma \equiv -\frac{1}{i_\sigma} F_\sigma^{-i_\sigma}$$

It is important to note that we cannot write $F_\sigma^{-1} \left\{ \frac{\partial}{\partial A} \right\} F_\sigma$ as the derivitive of ln F_σ

because the latter does not exist in the sense of a formal series. Thus we have

$$\langle (\underline{A}_\wedge \underline{F})\underline{F}^{-1-1} | \underline{X}^{-1} \rangle = \sum_{j} \varepsilon_{j_1 j_2 j_3} \langle \left(\left\{\frac{\partial}{A_{j_1}}\right\} G_1\right)\left(\frac{1}{F_2}\left\{\frac{\partial}{A_{j_2}}\right\}F_2\right)\left(\frac{1}{F_3}\left\{\frac{\partial}{A_{j_3}}\right\}F_3\right) | \underline{X}^{-1} \rangle$$

where $\varepsilon_{j_1 j_2 j_3}$ is the totally antisymmetric Levi-Civitia symbol. Now our expression equals

$$= \sum \varepsilon_{j_1 j_2 j_3} \langle \left\{\frac{\partial}{A_{j_1}}\right\}\left[G_1 \left(\frac{1}{F_2}\left\{\frac{\partial}{A_{j_2}}\right\}F_2\right)\left(\frac{1}{F_3}\left\{\frac{\partial}{A_{j_3}}\right\}F_3\right)\right] | \underline{X}^{-1} \rangle$$

$$- \sum \varepsilon_{j_1 j_2 j_3} \langle G_1 \left\{\frac{\partial}{A_{j_1}}\right\}\left[\left(\frac{1}{F_2}\left\{\frac{\partial}{A_{j_2}}\right\}F_2\right)\left(\frac{1}{F_3}\left\{\frac{\partial}{A_{j_3}}\right\}F_3\right)\right] | \underline{X}^{-1}$$

The first term is zero because the adjoint of the derivitive when acting on $\underline{x}^{-\underline{1}}$ automatically gives zero. The second term is likewise zero because the summand in the bra is proportional to

$$\left(\frac{1}{F_2}\left\{\frac{\partial}{A_{j_2}}\right\}F_2\right)\left(-\frac{1}{F_3^2}\left\{\frac{\partial}{A_{j_1}}\right\}F_3\left\{\frac{\partial}{A_{j_3}}\right\}F_3 + \frac{1}{F_3}\left\{\frac{\partial}{A_{j_1}}\right\}\left\{\frac{\partial}{A_{j_3}}\right\}F_3\right) + \text{SAME FORM WITH } 3 \leftrightarrow 2$$

which is symmetric in any two j's and so gives zero when summed over the Levi-Civitia symbol. The same arguments hold when any number of the i_σ are nonzero.

It is easy to see that when all the i_σ are zero we have

$$\frac{1}{F_\sigma}\left\{\frac{\partial}{A_\mu}\right\}F_\sigma = \delta_{\mu\sigma} A_\sigma^{-1} + \text{TERMS OF DEGREE MAGNITUDE} \geq 0$$

and so

$$(\underline{A}_\wedge \underline{F})\,\underline{F}^{-\underline{1}} = \underline{A}^{-\underline{1}} + \text{TERMS OF HIGHER DEGREE MAGNITUDE}$$

This shows that

$$\langle \underline{A}^{\underline{\ell}} | f_{\underline{\ell}} \rangle = \langle (\underline{A}_\wedge \underline{F})\underline{F}^{-\underline{1}} | \underline{X}^{-\underline{1}} \rangle = 1$$

which completes our proof.

To obtain the Lagrange formula in one variable we start by using the expansion theorem to express the bra element F(A) of degree zero ([F]=0) ad

$$F = \sum_{0}^{\infty} \frac{\langle F | \ell_K \rangle}{C_K} L^K$$

Taking the composition

$$F \circ \tilde{L} = \sum \frac{\langle F | \ell_K \rangle}{C_K} (L^K \circ \tilde{L})$$

yields

$$F(\tilde{L}) = \sum_{0}^{\infty} \frac{1}{c_K} \langle F \mid \ell_K \rangle A^K$$

By invoking the transfer formula in the limiting case of one variable we get

$$= \sum_{0}^{\infty} \frac{1}{c_K} \langle F \mid \frac{c_K}{c_{-1}} \left\{\frac{L'}{\partial}\right\}\left\{\frac{L}{\partial}\right\}^{-1-K} x^{-1} \rangle A^K$$

Here the prime stands for the formal derivitive of the series with respect to A. Taking adjoints yields

$$= \frac{1}{c_{-1}} \sum_{0}^{\infty} \langle F L' L^{-1-K} \mid x^{-1} \rangle A^K$$

Now consider the terms with $k \neq 0$. We have

$$\langle F L' L^{-1-K} \mid x^{-1} \rangle = -\frac{1}{K} \langle F (L^{-K})' \mid x^{-1} \rangle$$

$$= -\frac{1}{K} \langle (F L^{-K})' - F' L^{-K} \mid x^{-1} \rangle$$

$$= -\frac{1}{K} \langle F L^{-K} \mid \left\{\frac{A}{\partial}\right\} x^{-1} \rangle + \frac{1}{K} \langle F' L^{-K} \mid x^{-1} \rangle$$

$$= \frac{1}{K} c_{-1} \text{ Residue} (F' L^{-K})$$

Now consider the term k=0. We know that

$$L' L^{-1} = A^{-1} + \text{CONSTANT} + \text{TERMS OF HIGHER DEGREE}$$

so

$$\langle F L' L^{-1} \mid x^{-1} \rangle = F(0)\, c_{-1}$$

We thus obtain

$$F(\tilde{L}) = F(0) + \sum_{K=1}^{\infty} \frac{1}{K} \text{ Residue} (F' L^{-K}) A^K \qquad \text{EQU 3.1}$$

Which is seen to be the Lagrange-Burmann formula.

The multivariate formula follows upon expanding $F(\underline{A})$ in terms of $\underline{L}$, taking the composition with $\underline{\tilde{L}}$ and invoking the transfer formula:

$$F(\underline{\tilde{L}}) = \sum \frac{1}{\underline{c}_{\underline{1}}} \langle F(\underline{A}_\wedge \underline{L}) \underline{L}^{-\underline{1}-\underline{k}} \mid \underline{x}^{-\underline{1}} \rangle \, \underline{A}^{\underline{k}}$$

Other variants of the inversion theorem, for example theorems seven and eight of Good, follow directly from the transfer formula when one considers the system of equations

$$A_\sigma = \frac{D_\sigma}{F_\sigma(\underline{D})}$$

remembers that $(\underline{A}_\wedge\underline{D})(\underline{D}_\wedge\underline{A}) = 1$ and explicitly writes

$$(\underline{D}_\wedge \underline{A}) = \underline{F}^{-\underline{1}} \det \left(\delta_{\mu\nu} - \frac{D_\mu}{F_\mu} \left\{ \frac{\partial}{D_\nu} \right\} F_\mu \right)$$

4). The Reducible Cluster Coefficients

Our next application is to derive the relation between the reducible cluster coefficients $b_{\underline{n}}$ and the $\underline{n}$ body partition functions from the umbral formalism. This is alternatively known as Theile's moment-cumulant relations.

Recall from statistical mechanics that the grand partition function is given by

$$\Xi = \sum_{|\underline{i}|=0} Q_{\underline{i}}\, \underline{\lambda}^{\underline{i}} \qquad\qquad Q_{\underline{0}} \equiv 1$$

where $\lambda_\sigma = \exp u_\sigma$ with u_σ the chemical potential of the σ th species and $Q_{\underline{i}}$ is the partition function for i_α particles of species α, i_γ particles of species γ,etc. Following Hill's[11] notation we define

$$Z_{\underline{i}} \equiv \left(\frac{V}{Q_{e_\alpha}}\right)^{i_\alpha}\cdots\left(\frac{V}{Q_{e_\mu}}\right)^{i_\mu}(\underline{i}!)\,Q_{\underline{i}} \qquad\qquad A_\sigma \equiv \frac{Q_{e_\sigma}}{V}\lambda_\sigma$$

Then we can write the grand potential in the suggestive form

$$\sum_{|\underline{i}|=0} Z_{\underline{i}} \frac{\underline{A}^{\underline{i}}}{\underline{i}!} = \Xi \equiv e^{V\sum_{|\underline{i}|=1} b_{\underline{i}}\, \underline{A}^{\underline{i}}}$$

which defines the reducible cluster coefficients $b_{\underline{i}}$. We can write this compactly as

$$e^{VP} = 1 + F$$

where

$$P \equiv \sum_{|\underline{i}|=1} b_{\underline{i}}\, \underline{A}^{\underline{i}} \qquad\qquad F \equiv \sum_{|\underline{i}|=1} Z_{\underline{i}} \frac{\underline{A}^{\underline{i}}}{\underline{i}!}$$

For clarity of presentation we will proceed in the case of the single species gas. Because

$$\langle F|x^N\rangle = \langle e^{VP}-1\,|x^N\rangle = \sum_{k=1}^{\infty} \frac{1}{k!} \langle (VP)^k\,|x^N\rangle$$

we can use the product theorem to obtain

$$\langle F|x^N\rangle = \sum_{k=1}^{\infty}\frac{1}{k!}\sum_{\{j\}} \frac{C_N}{C_{j_1}C_{j_2}\cdots C_{j_k}} \langle VP|x^{j_1}\rangle\langle VP|x^{j_2}\rangle\cdots\langle VP|x^{j_k}\rangle$$

Remembering that

$$\langle VP\,|x^m\rangle = \begin{cases} Vm!\, b_m \\ 0 \end{cases} \qquad\qquad \langle F|x^m\rangle = \begin{cases} Z_m & \text{FOR } m>0 \\ 0 & \text{OTHERWISE} \end{cases}$$

we have

$$Z_N = \sum_{k=1}^{\infty} \frac{1}{k!} \sum_{\{j\}} N!\,(Vb_{j_1})(Vb_{j_2})\ldots(Vb_{j_k})$$

where the sum is over positive integer sets $j_1+j_2+\ldots j_k=N$. This sum can be rewritten as

$$Z_N = \sum_{k=1}^{\infty} \sum_{\{h\}} N!\, \frac{(Vb_1)^{h_1}}{h_1!} \frac{(Vb_2)^{h_2}}{h_2!} \frac{(Vb_3)^{h_3}}{h_3!} \cdots$$

where the sum is now over positive integer sets $\{h\}$ with the two restrictions

$$h_1+2h_2+3h_3+\ldots\ldots.=N$$

$$h_1+h_2+h_3+\ldots\ldots..=k$$

(We will make similar substitutions often in following applications.) We see that the summation over k nullifies the second constraint yielding the familiar result

$$Z_N = N! \sum_{\{h\}}' \prod_j \frac{(Vb_j)^{h_j}}{h_j!} \qquad \text{EQN 4.1}$$

The inverse relationship is easily derived using many of the same steps. We have

$$\langle VP|X^N\rangle = \langle \ln(1+F)|X^N\rangle = \sum_{j=1}^{\infty} \frac{(-1)^{j+1}}{j} \langle F^j|X^N\rangle$$

$$= \sum_{j=1}^{\infty} \frac{(-1)^{j+1}}{j} \sum_{\{k\}}' \frac{N!}{k_1!\,k_2!\ldots k_j!} \langle F|X^{k_1}\rangle \cdots \langle F|X^{k_j}\rangle$$

with the sum over positive integer sets $k_1+k_2+\ldots.k_j=N$. This easily gives

$$Vb_N = \sum_{1}^{\infty} \frac{(-1)^{j+1}}{j} \sum_{\{h\}} \frac{j!}{h_1!\,h_2!\ldots} \left(\frac{Z_1}{1!}\right)^{h_1}\left(\frac{Z_2}{2!}\right)^{h_2}\cdots$$

where the second sum is restricted by the two conditions

$$h_1+2h_2+3h_3+\ldots.=N$$

$$h_1+h_2+h_3+\ldots..=j$$

Again the latter restriction is removed by the summation over j. We thus obtain the familiar result

$$Vb_N = \sum_{\{h\}}' (-1)^{\sum_l h_l + 1} \left(\sum_l h_l - 1 \right)! \prod_l \frac{\left(\frac{B_l}{l!} \right)^{h_l}}{h_l!} \qquad \text{EQN 4.2}$$

The generalization to a multispecies gas follows completely analagous steps and only results in replacing the scalar indices in equations (4.1) and (4.2) with vector indices and replacing the constraining equation by

$$\sum_{\underline{m}}' \underline{m}\, h_{\underline{m}} = \underline{N}$$

5). One Species Virial Expansion

In this section we present the virial expansion and introduce the irreducible cluster coefficients for a single species gas.

Thermodynamic relations tells us that the pressure (divided by kT) and the density can be represented by the delta elements

$$P = b_1 A + b_2 A^2 + b_3 A^3 + \dots \qquad \text{EQN } 5.1$$

$$D = AP' = A\left\{\frac{\partial}{\partial A}\right\}P = 1b_1 A + 2b_2 A^2 + 3b_3 A^3 + \dots \qquad \text{EQN } 5.2$$

In all further manipulations we will explicitly use the value $b_1=1$.

The irreducible cluster coefficients β_k have three intimately related properties. First they are coefficients in the expansion of the pressure in terms of the density

$$P = D - \tfrac{1}{2}\beta_1 D^2 - \tfrac{2}{3}\beta_2 D^3 - \tfrac{3}{4}\beta_3 D^4 - \dots \qquad \text{EQN } 5.3$$

This property is a statement of the expansion theorem

$$P = \sum_{K=1}^{\infty} \frac{\langle P \mid \alpha_K \rangle}{K!} D^K$$

with

$$\frac{1}{K!}\langle P \mid \alpha_K \rangle = \begin{cases} 1 & \text{FOR } K=1 \\ -\frac{(K-1)}{K}\beta_{K-1} & K \geq 2 \end{cases} \qquad \text{EQN } 5.4$$

Secondly the reversion of the density (equation 5.2 gives the activity A as a function of density) can always be expressed in the form

$$A = D \exp -(\beta_1 D + \beta_2 D^2 + \beta_3 D^3 + \dots) \qquad \text{EQN } 5.5$$

In umbral formalism this property is that the compositional inverse can be expressed as

$$\tilde{D} = A e^{-M}$$

$$M = \beta_1 A + \beta_2 A^2 + \beta_3 A^3 + \dots$$

That is

$$\frac{1}{K!}\langle M \mid X^K \rangle = \beta_K \qquad \text{EQN } 5.6$$

Finally, by plugging equation (5.5) back into the activity expansion of the pressure we will obtain again the density expansion of the pressure,equation (5.3).

In umbral notation this property is expressed as

$$P \circ \tilde{D} = A - \tfrac{1}{2} B_1 A^2 - \tfrac{2}{3} B_2 A^3 - \dots$$

that is

$$\frac{1}{K!} \langle P \circ \tilde{D} \,|\, X^K \rangle = \begin{cases} 1 & \text{FOR } K = 1 \\ -\frac{(K-1)}{K} B_{K-1} & K \geq 2 \end{cases} \qquad \text{EQN 5.7}$$

The equivalence between equations (5.4) and (5.7) is easily established because

$$\langle P \,|\, d_K \rangle = \langle \left\{ \tfrac{A}{P} \right\}^{-1} A \,|\, \left\{ \tfrac{D}{A} \right\} X^K \rangle$$

$$= \langle \left\{ \tfrac{A}{P} \right\}^{-1} A \,|\, \left\{ \tfrac{\tilde{D}}{A} \right\}^{-1} X^K \rangle$$

$$= \langle \left\{ \tfrac{A}{\tilde{D}} \right\}^{-1} \left\{ \tfrac{A}{P} \right\}^{-1} A \,|\, X^K \rangle = \langle P \circ \tilde{D} \,|\, X^K \rangle$$

To demonstrate the equivalence between equations (5.4) and (5.6) we start from the relations

$$D = A \left\{ \tfrac{\partial}{\partial A} \right\} P \qquad \tilde{D} = A e^{-M}$$

We first take the composition

$$A = D \circ \tilde{D} = A e^{-M} \left(\left\{ \tfrac{\partial}{\partial A} \right\} P \right) \circ \tilde{D} = A e^{-M} \left\{ \tfrac{\partial}{\partial \tilde{D}} \right\} (P \circ \tilde{D})$$

then use the chain rule to find

$$\left\{ \tfrac{\partial}{\partial \tilde{D}} \right\} = \left(\left\{ \tfrac{\partial}{\partial \tilde{D}} \right\} A \right) \left\{ \tfrac{\partial}{\partial A} \right\} = \left(\left\{ \tfrac{\partial}{\partial A} \right\} \tilde{D} \right)^{-1} \left\{ \tfrac{\partial}{\partial A} \right\} = \left(e^{-M} - A e^{-M} \left\{ \tfrac{\partial}{\partial A} \right\} M \right)^{-1} \left\{ \tfrac{\partial}{\partial A} \right\}$$

and combine the two equations to obtain

$$\left\{ \tfrac{\partial}{\partial A} \right\} (P \circ \tilde{D}) = 1 - A \left\{ \tfrac{\partial}{\partial A} \right\} M$$

and so

$$\langle P \,|\, d_K \rangle = \langle P \circ \tilde{D} \,|\, X^K \rangle = \langle P \circ \tilde{D} \,|\, \left\{ \tfrac{A}{\partial} \right\} X^{K-1} \rangle = \langle \left\{ \tfrac{\partial}{\partial A} \right\} P \circ \tilde{D} \,|\, X^{K-1} \rangle \qquad \text{FOR } K \neq 0$$

$$= \langle A^0 - A \left\{ \tfrac{\partial}{\partial A} \right\} M \,|\, X^{K-1} \rangle$$

$$= \delta_{K,1} - \langle \left\{ \tfrac{\partial}{\partial A} \right\} M \,|\, \left\{ \tfrac{A}{\partial} \right\} X^{K-1} \rangle$$

$$= \delta_{K,1} - (K-1) \langle M | \{\tfrac{A}{\partial}\} x^{K-2} \rangle$$

$$= \delta_{K,1} - (K-1)(1-\delta_{K,1}) \langle M | x^{K-1} \rangle$$

Thus showing the desired equivalence.

We can express the pressure as a function of density in another form by writing

$$M = \{\tfrac{\partial}{A}\} S(A)$$

where

$$S(A) = \tfrac{1}{2} B_1 A^2 + \tfrac{1}{3} B_2 A^3 + \tfrac{1}{4} B_3 A^4 + \dots$$

is called the Mayer S function. If we start from the definition of density

$$P = \{\tfrac{\partial}{A}\}^{-1} (A^{-1} D)$$

$$= \{\tfrac{\partial}{D}\}^{-1} (\{\tfrac{\partial}{A}\} D)^{-1} \cdot (A^{-1} D)$$

$$= \{\tfrac{\partial}{D}\}^{-1} (\{\tfrac{\partial}{D}\} A) (A^{-1} D)$$

$$= \{\tfrac{\partial}{D}\}^{-1} \left(D^{\circ} - D \{\tfrac{\partial}{D}\} \ln(A^{-1} D) \right)$$

and using the fact that

$$A = \tilde{A} \circ D = (A e^{-M}) \circ D = D e^{-M \circ D}$$

we may substitute

$$\ln(A^{-1} D) = M \circ D$$

and so

$$P = \{\tfrac{\partial}{D}\}^{-1} (D^{\circ} - D \{\tfrac{\partial}{D}\} M \circ D)$$

$$= D - D(M \circ D) + \{\tfrac{\partial}{D}\}^{-1} (M \circ D)$$

$$= D - D(\{\tfrac{\partial}{A}\} S) \circ D + \{\tfrac{\partial}{D}\}^{-1} (\{\tfrac{\partial}{A}\} S) \circ D$$

$$= D - D \{\tfrac{\partial}{D}\} (S \circ D) + S \circ D$$

$$= D + S(D) - D \{\tfrac{\partial}{D}\} S(D)$$

6). The Reducible and Irreducible Cluster Coefficients

To express the irreducible cluster coefficients in terms of the reducible cluster coefficients for a single species gas we note that

$$\langle M | x^N \rangle = \langle M \cdot D | d_N \rangle = \langle \ln(A^{-1}D) | \left\{\frac{D}{\partial}\right\} d_{N-1} \rangle \qquad \text{FOR } N>0$$

$$= \langle \left\{\frac{\partial}{\partial D}\right\} \ln(A^{-1}D) | d_{N-1} \rangle = \langle A D^{-1} \left\{\frac{\partial}{\partial D}\right\} (A^{-1}D) | d_{N-1} \rangle$$

By the chain rule this becomes

$$= \langle A D^{-1} \left(\left\{\frac{\partial}{\partial A}\right\} D\right)^{-1} \left\{\frac{\partial}{\partial A}\right\} (A^{-1}D) | d_{N-1} \rangle$$

Upon invoking the transfer formula we obtain

$$= \langle A D^{-1} (D')^{-1} \left\{\frac{\partial}{\partial A}\right\} (A^{-1}D) | \left\{\frac{D'}{\otimes}\right\} \left\{\frac{A^{-1}D}{\otimes}\right\}^{-N} x^{N-1} \rangle$$

$$= \langle (A^{-1}D)^{-(N+1)} \left\{\frac{\partial}{\partial A}\right\} (A^{-1}D) | x^{N-1} \rangle$$

$$= -\frac{1}{N} \langle \left\{\frac{\partial}{\partial A}\right\} (A^{-1}D)^{-N} | x^{N-1} \rangle = -\frac{1}{N} \langle (A^{-1}D)^{-N} | \left\{\frac{A}{\partial}\right\} x^{N-1} \rangle$$

and so

$$\beta_N = \frac{1}{N!} \langle M | x^N \rangle = -\frac{1}{N} \frac{1}{N!} \langle (A^{-1}D)^{-N} | x^N \rangle$$

(This relation was postulated in the appendix of Kilpatricks paper [6] but heretofore never derived.) If we now define

$$F = (A^{-1}D) - 1$$

$$= 2b_2 A + 3b_3 A^2 + 4b_4 A^3 + \dots$$

giving us

$$\langle F | x^j \rangle = \begin{cases} (j+1)\, b_{j+1}\, (j!) & \text{FOR } j>0 \\ 0 & \text{OTHERWISE} \end{cases}$$

Then we have

$$\beta_N = -\frac{1}{N}\frac{1}{N!} < \left(\frac{1}{1+F}\right)^N | X^N >$$

$$= -\frac{1}{N}\frac{1}{N!} < \sum_{K=0}^{\infty} (-1)^K \frac{(N+K-1)!}{(N-1)!\,K!} F^K | X^N >$$

$$= \sum_{K=0}^{\infty} (-1)^{K+1} \frac{(N+K-1)!}{N!\,K!} \left(\frac{1}{N!} < F^K | X^N > \right)$$

Now

$$\frac{1}{N!} < F^K | X^N > = \frac{1}{N!} \sum_{\{j\}}' \frac{C_N}{C_{j_1} C_{j_2} \cdots C_{j_K}} < F | X^{j_1} > \cdots < F | X^{j_K} >$$

where the sum is over sets $j_1+j_2+\ldots.j_k=N$. This is equivalent to

$$\frac{1}{N!} < F^K | X^N > = \sum_{\{j\}}' [(j_1+1) b_{j_1+1}][(j_2+1) b_{j_2+1}] \cdots [(j_K+1) b_{j_K+1}]$$

$$= K! \sum_{\{h\}}' \frac{(2b_2)^{h_2}}{h_2!} \frac{(3b_3)^{h_3}}{h_3!} \frac{(4b_4)^{h_4}}{h_4!} \cdots$$

where the sum is now over sets such that

$$1h_1+2h_2+3h_3+\ldots..=N$$

$$h_1+h_2+h_3+\ldots\ldots.=k$$

Inserting into our formula for β_n the summation over k nullifies the second constraint and we are left with the familiar result

$$\beta_N = \sum_{\{h\}}' (-1)^{\sum_\ell h_\ell + 1} \frac{(N-1+\sum h_\ell)!}{N!} \prod_i \frac{(i b_i)^{h_i}}{h_i!}$$

The inverse relationship is easily derived using the Lagrange inversion formula (see equation 3.1 with F=A);

$$D = \sum_{j=1}^{\infty} \frac{1}{j} \frac{1}{C_{-1}} < B^{-j} | X^{-1} > A^j$$

Now as

$$X^{j-1} = \frac{C_{j-1}}{C_{-1}} \left\{ \frac{1}{\Phi} \right\}^{-j} X^{-1}$$

we obtain

$$D = \sum_{1}^{\infty} \frac{1}{j!} \langle (A^{-1}\delta)^{-j} \,|\, X^{j-1} \rangle A^{j}$$

inserting

$$\delta = A e^{-M}$$

we get

$$j!\,(j b_j) = \langle D \,|\, X^{j} \rangle = \langle e^{jM} \,|\, X^{j-1} \rangle$$

$$= \sum_{k=0}^{\infty} \frac{1}{k!} \langle (jM)^{k} \,|\, X^{j-1} \rangle$$

$$= \sum_{k=0}^{\infty} \frac{j^{k}}{k!} \sum_{\{p\}} \frac{C_{j-1}}{C_{p_1} C_{p_2} \cdots C_{p_k}} \langle M \,|\, X^{p_1} \rangle \cdots \langle M \,|\, X^{p_k} \rangle$$

with the sum over sets $p_1+p_2+\dots p_k=j-1$. This gives us

$$= \sum_{k=0}^{\infty} \frac{1}{k!} \sum_{\{p\}} (j-1)!\, (jB_{p_1})(jB_{p_2}) \cdots (jB_{p_k})$$

$$= \sum_{k=0}^{\infty} \sum_{\{h\}} (j-1)!\, \frac{(jB_1)^{h_1}}{h_1!} \frac{(jB_2)^{h_2}}{h_2!} \cdots$$

where the sum in now over sets such that

$$1h_1+2h_2+3h_3+\dots=j-1$$

$$h_1+h_2+h_3+\dots=k$$

However the summation over k nullifies the second constraint ,yielding the familiar result

$$b_j = \frac{1}{j^2} \sum_{\{h\}} \prod_{k} \frac{(jB_k)^{h_k}}{h_k!}$$

7). The Multispecies Virial Expansion

In this section we introduce the multivariable Mayer S function and derive the virial expansion for a multispecies gas. For illustrative purposes only certain steps will be presented for a two or three component gas, the generalization to any number of species being apparant.

Thermodynamic relations tells us that the pressure (divided by kT) and the densities of the individual species can be represented by the bra elements

$$P = \sum_{\underline{l}} b_{\underline{l}} A^{\underline{l}} = b_{10} A_\alpha^2 + b_{01} A_\gamma^2 + b_{20} A_\alpha^2 + b_{11} A_\alpha A_\gamma + b_{02} A_\gamma^2 + \cdots$$

$$D_\sigma = A_\sigma P_\sigma \equiv A_\sigma \left\{ \frac{\partial}{A_\sigma} \right\} P$$

In all further manipulations we will implicitly use the values $b_{\underline{e_\sigma}} = 1$. Note that the densities

$$D_\alpha = b_{10} A_\alpha + b_{11} A_\alpha A_\gamma + 2 b_{20} A_\alpha^2 + \cdots$$

$$D_\gamma = b_{01} A_\gamma + b_{11} A_\alpha A_\gamma + 2 b_{02} A_\gamma^2 + \cdots$$

form a delta set vector and so has a compositional inverse which is also a delta set vector. Such a compostional inverse can always be written in the form

$$\delta_\sigma = A_\sigma W_\sigma$$

where the degree magnitude of W_σ is zero. Now the property unique to our system which we shall prove is that

$$P_{\alpha|\gamma} = P_{\gamma|\alpha}$$

implies

$$W_\alpha^{-1} W_{\alpha|\gamma} = W_\gamma^{-1} W_{\gamma|\alpha}$$

where for shorthand we have adopted the notation $P_{\alpha|\gamma} \equiv \left\{ \frac{\partial}{A_\gamma} \right\} P_\alpha$ etc.

This being the case we can always write

$$W_\sigma = e^{-\left\{ \frac{\partial}{A_\sigma} \right\} S}$$

where S is the same function for all components σ. This function is known as the Mayer S function. Thermodynamic relations also tells us that this function is intimately related to the excess Helmholtz free energy.[3]

Now to show

$$D_\sigma = A_\sigma P_\sigma \longrightarrow \tilde{D}_\sigma = A_\sigma e^{-\left\{\frac{\partial}{A_\sigma}\right\}S}$$

we note that

$$W_\alpha^{-1} = A_\alpha \tilde{D}_\alpha^{-1} = (D_\alpha A_\alpha^{-1}) \circ \underline{\tilde{D}} = (P_\alpha) \circ \underline{\tilde{D}}$$

$$W_{\alpha|\gamma} = \left\{\frac{\partial}{A_\gamma}\right\}(A_\alpha^{-1}\tilde{D}_\alpha) = A_\alpha^{-1}\left\{\frac{\partial}{A_\gamma}\right\}\tilde{D}_\alpha = (D_\alpha^{-1} \circ \underline{\tilde{D}})\left(\left\{\frac{\partial}{A_\gamma}\right\}\tilde{D}_\alpha\right)$$

To express the last term as a compositon we let

$$\left\{\frac{\partial}{A_\gamma}\right\}\tilde{D}_\alpha = G \circ \underline{\tilde{D}}$$

thus

$$G = \left(\left\{\frac{\partial}{A_\gamma}\right\}\tilde{D}_\alpha\right) \circ \underline{D} = \left\{\frac{\partial}{D_\gamma}\right\}(\tilde{D}_\alpha \circ \underline{D}) = \left\{\frac{\partial}{D_\gamma}\right\} A_\alpha$$

so

$$W_{\alpha|\gamma} = (D_\alpha^{-1} \circ \underline{\tilde{D}})\left[\left(\left\{\frac{\partial}{D_\gamma}\right\}A_\alpha\right) \circ \underline{\tilde{D}}\right]$$

$$W_\alpha^{-1} W_{\alpha|\gamma} = \left(P_\alpha D_\alpha^{-1}\left\{\frac{\partial}{D_\gamma}\right\}A_\alpha\right) \circ \underline{\tilde{D}}$$

$$= \left(A_\alpha^{-1}\left\{\frac{\partial}{D_\gamma}\right\}A_\alpha\right) \circ \underline{\tilde{D}}$$

We thus need only show that the expression

$$A_\alpha^{-1}\left\{\frac{\partial}{D_\gamma}\right\}A_\alpha$$

is symmetric in the arguments α and γ . We illustrate this assertion as follows. From the chain rule we know that

$$\left\{\frac{\partial}{D_\alpha}\right\} = \left(\left\{\frac{\partial}{D_\alpha}\right\}A_\alpha\right)\left\{\frac{\partial}{A_\alpha}\right\} + \left(\left\{\frac{\partial}{D_\alpha}\right\}A_\gamma\right)\left\{\frac{\partial}{A_\gamma}\right\} + \left(\left\{\frac{\partial}{D_\alpha}\right\}A_\mu\right)\left\{\frac{\partial}{A_\mu}\right\}$$

$$\left\{\frac{\partial}{D_\gamma}\right\} = \left(\left\{\frac{\partial}{D_\gamma}\right\}A_\alpha\right)\left\{\frac{\partial}{A_\alpha}\right\} + \left(\left\{\frac{\partial}{D_\gamma}\right\}A_\gamma\right)\left\{\frac{\partial}{A_\gamma}\right\} + \left(\left\{\frac{\partial}{D_\gamma}\right\}A_\mu\right)\left\{\frac{\partial}{A_\mu}\right\}$$

$$\left\{\frac{\partial}{D_\mu}\right\} = \left(\left\{\frac{\partial}{D_\mu}\right\}A_\alpha\right)\left\{\frac{\partial}{A_\alpha}\right\} + \left(\left\{\frac{\partial}{D_\mu}\right\}A_\gamma\right)\left\{\frac{\partial}{A_\gamma}\right\} + \left(\left\{\frac{\partial}{D_\mu}\right\}A_\mu\right)\left\{\frac{\partial}{A_\mu}\right\}$$

This allows us to form the matrix equation

$$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} = \begin{pmatrix} \left\{\frac{\partial}{\partial D_\alpha}\right\} A_\alpha & \left\{\frac{\partial}{\partial D_\alpha}\right\} A_\gamma & \left\{\frac{\partial}{\partial D_\alpha}\right\} A_\mu \\ \left\{\frac{\partial}{\partial D_\gamma}\right\} A_\alpha & \left\{\frac{\partial}{\partial D_\gamma}\right\} A_\gamma & \left\{\frac{\partial}{\partial D_\gamma}\right\} A_\mu \\ \left\{\frac{\partial}{\partial D_\mu}\right\} A_\alpha & \left\{\frac{\partial}{\partial D_\mu}\right\} A_\gamma & \left\{\frac{\partial}{\partial D_\mu}\right\} A_\mu \end{pmatrix} \begin{pmatrix} \left\{\frac{\partial}{\partial A_\alpha}\right\} D_\alpha & \left\{\frac{\partial}{\partial A_\alpha}\right\} D_\gamma & \left\{\frac{\partial}{\partial A_\alpha}\right\} D_\mu \\ \left\{\frac{\partial}{\partial A_\gamma}\right\} D_\alpha & \left\{\frac{\partial}{\partial A_\gamma}\right\} D_\gamma & \left\{\frac{\partial}{\partial A_\gamma}\right\} D_\mu \\ \left\{\frac{\partial}{\partial A_\mu}\right\} D_\alpha & \left\{\frac{\partial}{\partial A_\mu}\right\} D_\gamma & \left\{\frac{\partial}{\partial A_\mu}\right\} D_\mu \end{pmatrix}$$

or in matrix symbols $\underline{1} = \underline{\underline{E}}\,\underline{\underline{G}}$. Now the matrix $\underline{\underline{G}}$ has the property

$$G = \begin{pmatrix} P_{\alpha|\alpha} + A_\alpha^{-1} P_\alpha & P_{\gamma|\alpha} & P_{\mu|\alpha} \\ P_{\alpha|\gamma} & P_{\gamma|\gamma} + A_\gamma^{-1} P_\gamma & P_{\mu|\gamma} \\ P_{\alpha|\mu} & P_{\gamma|\mu} & P_{\mu|\mu} + A_\mu^{-1} P_\mu \end{pmatrix} \begin{pmatrix} A_\alpha & 0 & 0 \\ 0 & A_\gamma & 0 \\ 0 & 0 & A_\mu \end{pmatrix}$$

or in matrix symbols $\underline{\underline{G}} = \underline{\underline{H}}\,\underline{\underline{U}}$ where $\underline{\underline{H}}^T = \underline{\underline{H}}$ is a symmetric matrix.

Now what we have to show is $A_j^{-1}(\underline{\underline{E}})_{ij}$ is symmetric in the indices i and j. Because

$$(\underline{\underline{E}})_{ij} = (\underline{\underline{G}}^{-1})_{ij} = (\det \underline{\underline{G}})^{-1}(-1)^{i+j} \det \underline{\underline{G}}_{(ji)}$$

(where $\underline{\underline{G}}_{(ji)}$ is the matrix formed by deleting the j th row and i th column of $\underline{\underline{G}}$)we need only show that

$$A_j^{-1} \det \underline{\underline{G}}_{(ji)}$$

is symmetric in i and j. We note that because of its structure (ie $\underline{\underline{G}} = \underline{\underline{H}}\,\underline{\underline{U}}$) we have

$$\det \underline{\underline{G}}_{(ji)} = (A_i^{-1} \det \underline{\underline{U}})(\det \underline{\underline{H}}_{(ji)})$$

The final argument is that for a symmetric matrix $\underline{\underline{H}}_{(ij)} = \underline{\underline{H}}_{(ji)}^T$, that is striking row i and column j and transposing is the same as striking row j and column i. Now because

$$\det \underline{\underline{F}} = \det(\underline{\underline{F}}^T)$$

we obtain our desired symmetry.

From the form of the compositional inverse of the density

$$\tilde{D}_\sigma = A_\sigma e^{-\left\{\frac{\partial}{\partial A_\sigma}\right\} S(\underline{A})}$$

we can proceed to the virial expansion by taking the composition with $\underline{D}$

$$A_\sigma = D_\sigma e^{-\left(\left\{\frac{\partial}{\partial A_\sigma}\right\} S\right) \circ \underline{D}} = D_\sigma e^{-\left\{\frac{\partial}{\partial D_\sigma}\right\} (S \circ \underline{D})}$$

$$\ln D_\sigma = \ln A_\sigma + \left\{\frac{\partial}{\partial D_\sigma}\right\} (S \circ \underline{D})$$

and so for any component index μ we may write

$$1 = \sum_\sigma D_\sigma \left\{\frac{\partial}{\partial D_\mu}\right\} \left[\ln A_\sigma + \left\{\frac{\partial}{\partial D_\sigma}\right\} (S \circ \underline{D})\right]$$

Inserting the fact that

$$\frac{D_\sigma}{A_\sigma} = \left\{\frac{\partial}{\partial A_\sigma}\right\} P$$

we have

$$1 = \sum_\sigma \left(\left\{\frac{\partial}{\partial D_\mu}\right\} A_\sigma\right)\left(\left\{\frac{\partial}{\partial A_\sigma}\right\} P\right) + \sum_\sigma \left\{\frac{\partial}{\partial D_\mu}\right\} \left(D_\sigma \left\{\frac{\partial}{\partial D_\sigma}\right\} S \circ \underline{D}\right) - \left(\left\{\frac{\partial}{\partial D_\sigma}\right\} S \circ \underline{D}\right)\left\{\frac{\partial}{\partial D_\mu}\right\}$$

$$1 = \left\{\frac{\partial}{\partial D_\mu}\right\} \left[P + \sum_\sigma D_\sigma \left\{\frac{\partial}{\partial D_\sigma}\right\} (S \circ \underline{D}) - S \circ \underline{D}\right]$$

Because this is true for any μ and constrained by the boundary conditions $P \to 0$ as $\underline{D} \to 0$ we obtain the unique solution

$$P = \sum_\sigma D_\sigma - \sum_\sigma D_\sigma \left\{\frac{\partial}{\partial D_\sigma}\right\} S(\underline{D}) + S(\underline{D})$$

If we define the irreducible cluster coefficients $B_{\underline{n}}$ by the expansion

$$S(\underline{A}) = \sum_{|\underline{N}| \geq 2}^{\prime} B_{\underline{N}} \underline{A}^{\underline{N}}$$

we obtain the familiar multispecies virial expansion

$$P = \sum_\sigma D_\sigma - \sum_{|\underline{N}| \geq 2}^{\prime} (\underline{N} \cdot \underline{1} - 1) B_{\underline{N}} \underline{D}^{\underline{N}}$$

8). The Irreducible Cluster Coefficients

We now present the relations between the reducible and irreducible cluster coefficients for a multispecies gas. We will express the reducible coefficients in terms of the irreducible in a manner that yields the same results as contained in Fuch's[3] paper. A comparison of the two methods is appropriate. The irreducible coefficients in terms of the reducible has never been presented before.

Starting with the knowledge

$$D_\alpha = A_\alpha P_\alpha \longrightarrow \tilde{D}_\alpha = A_\alpha W_\alpha$$

we invoke the transfer formula to obtain

$$\langle D_\alpha | \underline{x}^{\underline{\ell}} \rangle = \langle A_\alpha | \tilde{d}_{\underline{\ell}} \rangle = \langle A_\alpha (\underline{\Delta}_\wedge \underline{A}\underline{W})\, \underline{W}^{-1-\underline{\ell}} | \underline{x}^{\underline{\ell}} \rangle = \frac{C_{\underline{\ell}}}{C_{\underline{\ell}-\underline{e}_\alpha}} \langle (\underline{\Delta}_\wedge \underline{A}\underline{W})\, \underline{W}^{-1-\underline{\ell}} | \underline{x}^{\underline{\ell}-\underline{e}_\alpha} \rangle$$

Now because $W_\sigma = \exp - S_\sigma$ where $S_\sigma = \left\{\frac{\partial}{A_\sigma}\right\} S$, that is $S_{\alpha|\gamma} = S_{\gamma|\alpha}$, we may write

$$(\underline{\Delta}_\wedge \underline{A}\underline{W})\, \underline{W}^{-1-\underline{\ell}} = \begin{vmatrix} W_\alpha^{-\ell_\alpha}\left(1 + A_\alpha \left\{\frac{\partial}{A_\alpha}\right\} \ln W_\alpha\right) & W_\alpha^{-\ell_\alpha}\left(A_\gamma \left\{\frac{\partial}{A_\alpha}\right\} \ln W_\gamma\right) & \cdots \\ W_\gamma^{-\ell_\gamma}\left(A_\alpha \left\{\frac{\partial}{A_\gamma}\right\} \ln W_\alpha\right) & W_\gamma^{-\ell_\gamma}\left(1 + A_\gamma \left\{\frac{\partial}{A_\gamma}\right\} \ln W_\gamma\right) & \cdots \\ \vdots & \vdots & \end{vmatrix}$$

$$= \begin{vmatrix} \left(1 - \frac{A_\alpha}{\ell_\alpha} \left\{\frac{\partial}{A_\alpha}\right\}\right) e^{\ell_\alpha S_\alpha} & \left(- \frac{A_\gamma}{\ell_\alpha} \left\{\frac{\partial}{A_\gamma}\right\}\right) e^{\ell_\alpha S_\alpha} & \cdots \\ \left(- \frac{A_\alpha}{\ell_\gamma} \left\{\frac{\partial}{A_\alpha}\right\}\right) e^{\ell_\gamma S_\gamma} & \left(1 - \frac{A_\gamma}{\ell_\gamma} \left\{\frac{\partial}{A_\gamma}\right\}\right) e^{\ell_\gamma S_\gamma} & \cdots \\ \vdots & \vdots & \end{vmatrix}$$

This simplification of the transfer formula allows us to arrive at the equivalent of Fuch's[3] equation 4.5, namely

$$\ell_\alpha b_{\underline{\ell}} = \frac{1}{C_{\underline{\ell}-\underline{e}_\alpha}} \left\langle \det\left(\left(\delta_{ij} - \frac{A_i}{\ell_j}\left\{\frac{\partial}{A_i}\right\}\right) e^{\ell_j S_j}\right) \middle| \underline{x}^{\underline{\ell}-\underline{e}_\alpha} \right\rangle$$

To evaluate the right hand side explicitly we use the totally antisymmetric Levi-Civitia symbol in μ dimensions to expand the determinant and then invoke the product theorem to obtain

$$\ell_\alpha b_{\underline{\ell}} = \sum_i{}' \epsilon_{i_1 \ldots i_\mu} \sum_{\{\underline{k}\}}{}' \frac{\langle (\delta_{i_1 1} - \frac{A_{i_1}}{\ell_1}\{\frac{\partial}{\partial A_{i_1}}\}) e^{\ell_1 S_1} | \underline{x}^{\underline{k}^{(1)}} \rangle}{C_{\underline{k}^{(1)}}} \cdots \frac{\langle (\delta_{i_\mu \mu} - \frac{A_{i_\mu}}{\ell_\mu}\{\frac{\partial}{\partial A_{i_\mu}}\}) e^{\ell_\mu S_\mu} | \underline{x}^{\underline{k}^{(\mu)}} \rangle}{C_{\underline{k}^{(\mu)}}}$$

Here the second sum is over all sets of vectors $\underline{k}^{(i)}$ satisfying

$$\underline{k}^{(1)} + \underline{k}^{(2)} + \ldots\ldots \underline{k}^{(\mu)} = \underline{\ell} - \underline{e_\alpha}$$

Now it is easily worked out that

$$\langle (\delta_{i_1 1} - \frac{A_{i_1}}{\ell_1}\{\frac{\partial}{\partial A_{i_1}}\}) e^{\ell_1 S_1} | \underline{x}^{\underline{k}^{(1)}} \rangle = \delta_{i_1 1} \langle e^{\ell_1 S_1} | \underline{x}^{\underline{k}^{(1)}} \rangle - \frac{1}{\ell_1} \langle A_{i_1}\{\frac{\partial}{\partial A_{i_1}}\} e^{\ell_1 S_1} | \underline{x}^{\underline{k}^{(1)}} \rangle$$

$$= \text{"} \qquad \text{"} - \frac{1}{\ell_1} \langle \{\frac{\partial}{\partial A_{i_1}}\} e^{\ell_1 S_1} | \cdot \frac{C_{\underline{k}^{(1)}}}{C_{\underline{k}^{(1)} - \underline{e_{i_1}}}} \underline{x}^{\underline{k}^{(1)} - \underline{e_{i_1}}} \rangle$$

$$= \text{"} \qquad \text{"} - \frac{1}{\ell_1} \frac{C_{\underline{k}^{(1)}}}{C_{\underline{k}^{(1)} - \underline{e_{i_1}}}} \langle e^{\ell_1 S_1} | \underline{x}^{\underline{k}^{(1)}} \rangle \qquad \text{FOR } K^{(1)}_{i_1} \neq 0$$

$$= (\delta_{i_1 1} - \frac{K^{(1)}_{i_1}}{\ell_1}) \langle e^{\ell_1 S_1} | \underline{x}^{\underline{k}^{(1)}} \rangle$$

with the same result for different indices with the other factors. This allows us to write

$$\ell_\alpha b_{\underline{\ell}} = \sum_{\{\underline{k}\}}{}' \det(\delta_{ij} - \frac{K^{(j)}_i}{\ell_j}) \frac{\langle e^{\ell_1 S_1} | \underline{x}^{\underline{k}^{(1)}} \rangle}{C_{\underline{k}^{(1)}}} \cdots \frac{\langle e^{\ell_\mu S_\mu} | \underline{x}^{\underline{k}^{(\mu)}} \rangle}{C_{\underline{k}^{(\mu)}}}$$

Using the product rule we can explicitly compute the factors

$$< e^{\ell_\alpha S_\alpha} | \underline{x}^{\underline{k}} > = \sum_{p=0}^{\infty} \frac{1}{p!} < (\ell_\alpha S_\alpha)^p | \underline{x}^{\underline{k}} >$$

$$= \sum_{p=0}^{\infty} \frac{1}{p!} \sum_{\{\underline{m}\}} c_{\underline{k}} \frac{<\ell_\alpha S_\alpha | \underline{x}^{\underline{m}^{(1)}}>}{c_{\underline{m}^{(1)}}} \cdots \frac{<\ell_\alpha S_\alpha | \underline{x}^{\underline{m}^{(p)}}>}{c_{\underline{m}^{(p)}}}$$

where the sum is over all sets of vectors $\underline{m}^{(i)}$ such that

$$\underline{m}^{(1)}+\underline{m}^{(2)}+\ldots\ldots+\underline{m}^{(p)}= \underline{k}$$

We can easily reexpress this as

$$= c_{\underline{k}} \sum_{p=0}^{\infty} \sum_{\{h\}}' \prod_{\underline{m}} \frac{[(\ell_\alpha)(m_\alpha+1) B_{\underline{m}+\underline{e}_\alpha}]^{h_{\underline{m}}}}{h_{\underline{m}}!}$$

where the second sum is now over all sets of integers $h_{\underline{m}}$ which satisfies the two constraint.

$$\sum_{\underline{m}} h_{\underline{m}} = p$$

$$\sum_{\underline{m}} \underline{m}\, h_{\underline{m}} = \underline{k}$$

The first sum over p eliminates the first constraint leaving

$$\frac{< e^{\ell_\alpha S_\alpha} | \underline{x}^{\underline{k}^{(\alpha)}} >}{c_{\underline{k}^{(\alpha)}}} = \sum_{\{h^{(\alpha)}\}}' \prod_{\underline{m}} \frac{[(m_\alpha+1)(\ell_\alpha) B_{\underline{m}+\underline{e}_\alpha}]^{h_{\underline{m}}^{(\alpha)}}}{h_{\underline{m}}^{(\alpha)}!}$$

$$\sum_{\underline{m}} \underline{m}\, h_{\underline{m}}^{(\alpha)} = \underline{k}^{(\alpha)}$$

Inserting this result into our formula for the $b_{\underline{l}}$ yields Fuch's[8] equations 3.21 and 3.22, namely

$$\ell_\alpha b_{\underline{\ell}} = \sum_{\{h\}} \det\left(\delta_{ij} - \frac{1}{\ell_j} \sum_{\underline{m}} m_i h_{\underline{m}}^{(j)}\right) \prod_{\alpha=1}^{M} \prod_{\underline{m}} \frac{\left[(\ell_\alpha)(M_\alpha+1) B_{\underline{m}+\underline{e}_\alpha}\right]^{h_{\underline{m}}^{(\alpha)}}}{h_{\underline{m}}^{(\alpha)}!}$$

with the sum over all sets of integers $h_{\underline{m}}^{(\alpha)}$ satisfying

$$\sum_{\alpha=1}^{M} \sum_{\underline{m}} \underline{m}\, h_{\underline{m}}^{(\alpha)} = \underline{\ell} - \underline{e}_\alpha$$

To express the irreducible cluster coefficients in terms of the reducible we again start from the knowledge

$$\tilde{D}_\sigma = A_\sigma e^{-S_\sigma} \qquad D_\sigma = A_\sigma P_\sigma$$

where $S_\sigma = \left\{\frac{\partial}{\partial A_\sigma}\right\} S$ and $P_\sigma = \left\{\frac{\partial}{\partial A_\sigma}\right\} P$. For notational convenience we define the vector

$$\underline{P} = (P_\alpha, P_\gamma, \ldots, P_\mu)$$

We must implicitly remember that this vector is not a delta set vector.

By taking the composition

$$A_\sigma = \tilde{D}_\sigma \circ \underline{P} = (A_\sigma e^{-S_\sigma}) \circ \underline{P} = D_\sigma e^{-S_\sigma \circ \underline{P}}$$

we find

$$\langle S_\sigma \circ \underline{P} \mid d_{\underline{\ell}} \rangle = \langle \ln(A_\sigma^{-1} D_\sigma) \mid d_{\underline{\ell}} \rangle$$

Invoking the transfer formula leads to

$$\langle S_\sigma \mid \underline{x}^{\underline{\ell}} \rangle = \langle \ln P_\sigma \, (\underline{\Delta}_\wedge \underline{\Delta P}) \, \underline{P}^{-1-\underline{\ell}} \mid \underline{x}^{\underline{\ell}} \rangle$$

We may simplify the transfer formula because $P_{\alpha|\gamma} = P_{\gamma|\alpha}$ allows us to write

$$(\underline{A}_\wedge \underline{AP})\,\underline{P}^{-1-\underline{\ell}} = \begin{vmatrix} \left(1-\frac{A_\alpha}{\ell_\alpha}\left\{\frac{\partial}{A_\alpha}\right\}\right)P_\alpha^{-\ell_\alpha} & \left(-\frac{A_\gamma}{\ell_\alpha}\left\{\frac{\partial}{A_\gamma}\right\}\right)P_\alpha^{-\ell_\alpha} & \cdots \\ \left(-\frac{A_\alpha}{\ell_\gamma}\left\{\frac{\partial}{A_\alpha}\right\}\right)P_\gamma^{-\ell_\gamma} & \left(1-\frac{A_\gamma}{\ell_\gamma}\left\{\frac{\partial}{A_\gamma}\right\}\right)P_\gamma^{-\ell_\gamma} & \cdots \\ \vdots & \vdots & \end{vmatrix}$$

$$= \det\left[\left(\delta_{ij} - \frac{A_i}{\ell_j}\left\{\frac{\partial}{A_i}\right\}\right)P_j^{-\ell_j}\right]$$

Following the same steps used in deriving the inverse relation we obtain

EQN 8.1

$$(\ell_\sigma+1)\,B_{\underline{\ell}+\underline{e}_\sigma} = \sum_{\{\underline{k}\}}' \det\left(\delta_{ij} - \frac{k_i^{(j)}}{\ell_j}\right) \frac{\langle P_1^{-\ell_1}|\underline{X}^{\underline{k}^{(1)}}\rangle}{C_{\underline{k}^{(1)}}} \cdots \frac{\langle P_\mu^{-\ell_\mu}|\underline{X}^{\underline{k}^{(\mu)}}\rangle}{C_{\underline{k}^{(\mu)}}} \frac{\langle \ln P_\sigma|\underline{X}^{\underline{k}^{(0)}}\rangle}{C_{\underline{k}^{(0)}}}$$

The summation is over all sets of vectors $\underline{k}^{(i)}$ such that

$$\underline{k}^{(0)}+\underline{k}^{(1)}+\underline{k}^{(2)}+\ldots\underline{k}^{(\mu)}=\underline{\ell}$$

while the indices i and j in the determinant run from 1 to μ.

Each of the individual brackets are also calculable from the product rule, for example

$$\frac{\langle P_j^{-\ell_j}|\underline{X}^{\underline{k}}\rangle}{C_{\underline{k}}} \equiv \frac{1}{C_{\underline{k}}}\langle (1+R_j)^{-\ell_j}|\underline{X}^{\underline{k}}\rangle$$

$$= \sum_{m=0}^{\infty}(-1)^m \frac{(\ell_j+m-1)!}{(\ell_j-1)!\,m!} \frac{\langle R_j^m|\underline{X}^{\underline{k}}\rangle}{C_{\underline{k}}}$$

$$= \sum_{m=0}^{\infty}(-1)^m \frac{(\ell_j+m-1)!}{(\ell_j-1)!\,m!} \sum_{\{\underline{N}\}}' \frac{\langle R_j|\underline{X}^{\underline{N}^{(1)}}\rangle}{C_{\underline{N}^{(1)}}} \cdots \frac{\langle R_j|\underline{X}^{\underline{N}^{(m)}}\rangle}{C_{\underline{N}^{(m)}}}$$

with $\underline{N}^{(1)}+\underline{N}^{(2)}+\ldots\ldots+\underline{N}^{(m)}=\underline{k}$

Familiar manipulations yield the result

$$\frac{\langle P_s^{-\ell_s} \mid \underline{X}^{\underline{k}^{(s)}} \rangle}{C_{\underline{k}^{(s)}}} = \sum_{\{h^{(s)}\}}' (-1)^{\Sigma h_{\underline{r}}^{(s)}} \frac{(\ell_s + \Sigma h_{\underline{r}}^{(s)} - 1)!}{(\ell_s - 1)!} \prod_{\underline{r}} \frac{[(r_s+1)\, b_{\underline{r}} + \underline{e}_s]^{h_{\underline{r}}^{(s)}}}{h_{\underline{r}}^{(s)}!}$$

with the sum restricted over integer sets such that

$$\sum_{\underline{r}} \underline{r}\, h_{\underline{r}}^{(s)} = \underline{k}^{(s)} .$$

Likewise we find

$$\frac{\langle \ln P_\sigma \mid \underline{X}^{\underline{k}^{(\sigma)}} \rangle}{C_{\underline{k}^{(\sigma)}}} = \sum_{\{h^{(\sigma)}\}} (-1)^{\Sigma h_{\underline{r}}^{(\sigma)} + 1} (\Sigma h_{\underline{r}}^{(\sigma)} - 1)! \prod_{\underline{r}} \frac{[(r_\sigma+1)\, b_{\underline{r}} + \underline{e}_\sigma]^{h_{\underline{r}}^{(\sigma)}}}{h_{\underline{r}}^{(\sigma)}!}$$

with

$$\sum_{\underline{r}} \underline{r}\, h_{\underline{r}}^{(\sigma)} = \underline{k}^{(\sigma)}$$

Although quite complicated these results when inserted into equation (8.1) give the desired explicit relation between the $B_{\underline{n}}$ in terms of the $b_{\underline{j}}$.

9). Conclusion

It has hopefully been shown that the umbral calculus provides a simple method of obtaining quite complicated results. Doubtless the tools of umbral calculus may present simpler forms of the relations between the multispecies $B_{\underline{n}}$ and $b_{\underline{n}}$ than those originally derived by Fuchs or presented here, but this has not been pursued.

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